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STUDIES IN SILAZANE CHEMISTRY

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ABSTRACT

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The chemistry of a number of silazane compounds has been studied in an effort to prepare polymers containing Si-N linkages. This effort has resulted in the discovery or development of some new and interesting polymeric materials.

Polysilazanes having good thermal stability, elastomeric properties, and good film-forming properties have been prepared. A method has been developed for the preparation of an elastomeric silazane from dimethyldichlorosilane and ethylenediamine. This material has good thermal stability and remains rubbery after extended exposure to elevated temperatures (300-400°C).

Polymers having a number of useful properties were prepared by the polymerization of equimolar amounts of hexaphenylcyclotri-silazane and a number of different aromatic diols such as p, p'-biphenol.

Author

ACKNOWLEDGMENT

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NASA-GEORGE C. MARSHALL SPACE FLIGHT CENTER

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STUDIES IN SILAZANE CHEMISTRY

SUMMARY

During recent years, a considerable interest has developed in silazane chemistry--the chemistry of silicon-nitrogen compounds. A primary reason for this interest is the isosteric relationship between the Si-O linkage of silicones and the Si-NH linkage of the silazanes, which implies that there should be certain parallels in their chemical behavior. The silicones have found many uses such as lubricants, elastomers, and coatings.

This report summarizes the status of an internal study of the chemistry of silazanes and of materials produced by various reactions of silazanes. Most of this internal work was done in connection with and in support of contract NAS8-1510 with Southern Research Institute.

These combined efforts have shown that polysilazanes have many interesting properties, including good thermal stability and good film-forming properties, especially with respect to their stability in extreme environments. Certain polysilazanes can be prepared as weak elastomers in a one-step polymerization. These elastomer gums have potentially useful properties after thermal curing.

INTRODUCTION

Silicones in their various forms have found wide application in materials and chemical technology. They have shown many improved properties in comparison to conventional organic materials. However, they have certain limitations. Specifically, they are limited in their utility at high and low temperature extremes. Generally, silicones do not withstand prolonged exposure at temperatures above 250°C (482°F), and the best silicone elastomers become rigid at approximately -130°C (-202°F).

Since the N-H group of the silazane is isoelectronic with the silicon oxygen atom, it seems logical that the silazanes should be studied in an effort to obtain materials with improved properties. The silazane offers the potential advantage of being able to react or crosslink at the

hydrogen atom which is attached to the nitrogen atom. Another theoretical advantage of the silazanes is the $d\pi - p\pi$ interaction between the silicon and nitrogen atoms. This results from the ability of the "unshared" pair of electrons of the nitrogen atom to interact with the empty d orbitals of the silicon which causes a shorter bond distance. This is also an advantage in terms of chemical stability because the Si-N bond is rendered less subject to nucleophilic attack in many cases.

Some of the silazanes tend to be hydrolytically unstable. However, with the proper substituents attached to the silicon and nitrogen atoms, the $d\pi - p\pi$ bonding character may be increased, thus increasing the hydrolytic stability. By the use of suitable processing and curing techniques, this instability may also be minimized.

STATE-OF-THE-ART

The study of silicon-nitrogen compounds dates back to 1889 when Reynolds (Ref. 1) reported the preparation of tetraaminosilanes. However, the bulk of the work on polymeric silicon-nitrogen compounds has been done within the past 20 years. During this period, the interest in compounds of this type has become extensive. In 1961, Fessenden and Fessenden (Ref. 2) published a comprehensive review of silicon-nitrogen chemistry which cited a total of 221 references on these materials. Concurrently, a considerable interest has developed in producing polymers containing silicon-nitrogen units. In 1959, Henglein and Lienhard (Ref. 3) reported polymers of the type $[\text{Si}(\text{CH}_3)_2 - \text{NH}(\text{CH}_2)_x - \text{NH}]_n$, prepared from the reaction of dimethyldichlorosilane with various diamines. Also, shortly afterwards, Minner and Rochow (Ref. 4) independently reported the same polymer and showed how it coordinates with several metal chlorides. In the meantime, work was funded by this organization (starting in 1959 as a U. S. Army contract) to investigate methods of preparing polymers containing silicon-nitrogen bonds (Ref. 5). This effort resulted in the development of some interesting materials, and it has been continued and expanded (Contract NAS8-1510) (Ref. 6).

To supplement and assimilate the work done under contract to us, an internal investigation on silicon-nitrogen polymers has been conducted within our own laboratory. This report summarizes the present status of our work in relation to the contracted program.

EXPERIMENTAL

Study of Hexaphenylcyclotrisilazane

Burks and coworkers (Ref. 5 and 7) found that certain cyclic silazanes, such as hexaphenylcyclotrisilazane, may be polymerized to infusible polymers with exceptional thermal and chemical stability. In an effort to learn more about the complex high temperature reactions leading to the formation of this intractable polymer, hexaphenylcyclotrisilazane was investigated by differential thermal analysis (DTA) and thermogravimetric analysis (TGA).

The thermal behavior of hexaphenylcyclotrisilazane as revealed by TGA is compared to that of the corresponding siloxane in FIG 1. DTA studies of the same two materials are shown in FIG 2 and 3.

The good thermal stability of the ultimate product and the strong endothermic character of the high temperature reactions of hexaphenylcyclotrisilazane indicate that this material may be a useful component of ablative or intumescent coatings.

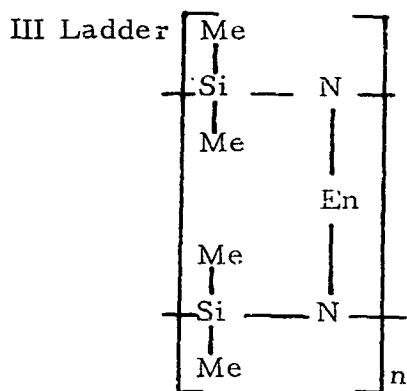
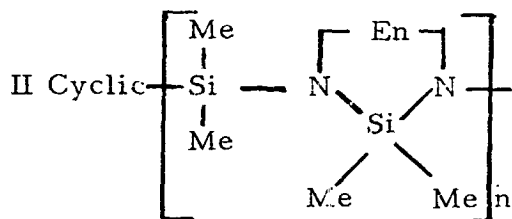
Several tests have been made to assess the performance of this material in heat barriers. Six samples containing varying amounts of hexaphenylcyclotrisilazane were tested by exposure to a radiant lamp at 24 BTU/ft²/sec for 120 seconds while being vibrated at 30 cycles per second with displacement of 0.25 inch with an acceleration of 11 times gravity.

The back-face temperature rise was measured as an indication of the materials performance. The samples were prepared by Southern Research Institute under Contract NAS8-1510 (Ref. 6), and tests were made at this Center. The compositions of the test samples are shown in Table I, and the test results are given in Table II. It is evident that some improvement resulted since the back-face temperature after 120 seconds was only 62.2°C for the sample with 25% hexaphenylcyclotrisilazane as compared to 90.0°C for the sample containing no silazane.

Diamine-Silazane Polymer

Extensive effort (Ref. 3, 4, 5, 8, 9, 10, 11, 12, 13, and 14) has been expended on the study of dichlorosilane-organic diamine copolymerization reactions.

The reaction product of ethylene diamine, $\text{En}(\text{NH}_2)_2$, and dimethyldichlorosilane, Me_2SiCl_2 , has been studied extensively; three polymeric structures are possible:



Minne' and Rochow (Ref. 4) originally reported that the linear form is first obtained and that it can be converted to the ladder form by refluxing in the presence of copper (II) chloride or beryllium chloride. However, in a later report (Ref. 15), Kruger and Rochow report that these polymers contain five-membered ring systems (Type II) which are connected by silicon atoms rather than having the exclusive linear structure (Ref. 10). Breed and coworkers (Ref. 11, 13, and 14) have reported polymers which are believed to have the cyclic configuration, and they have actually isolated monomeric species containing the five-membered ring moiety. In all of these cases, it was necessary to perform a two- or three-step reaction to obtain a product having an analysis which suggested the linear and/or cyclic structure.

Our work has led to a one-step method for obtaining what appears to be a high proportion of cyclic and/or ladder polymer configuration. It was found that the reaction of a 1:1:2 molar ratio of dimethyldichlorosilane, ethylenediamine, and triethylamine produced a spongy elastomeric polymer during the initial step. A typical reaction was conducted by adding 0.2 mole of dimethyldichlorosilane and 200 ml of dry benzene to a one-liter, three-neck flask which was equipped with a stirrer, dropping funnel, and reflux condenser. A separate solution was prepared containing 0.2 mole of ethylenediamine and 0.4 mole of triethylamine in 100 ml of dry benzene. The mixed amine solution was added by drops over a 90-minute period to the halosilane. The resulting solution was then refluxed for a period of 3-1/2 hours. The triethylamine hydrochloride was removed by filtration, and the benzene was removed under reduced pressure. This gave 97% yield of a spongy yellow solid polymer. The calculated analyses of the three possible polymer forms compared to experimental values are shown below:

	Calculated Values			Actual Experimental
	Linear	Cyclic	Ladder	
% Nitrogen	24.10	16.25	16.25	16.8
% Silicon	24.16	32.59	32.59	31.5

The carbon and hydrogen contents of all three forms are so close that they are valueless for characterization purposes, and the situation is complicated further because the cyclic and ladder forms have identical silicon and nitrogen contents. Thus, it can be inferred only that this particular polymer was comprised largely of cyclic and/or ladder units. The elastomeric nature of the product suggests strongly that appreciable ladder-type bridges occurred as crosslinks between chains. However, it is concluded that the use of triethylamine as an acid acceptor in the above system produced a polymer with potentially useful elastomeric properties.

To compare the properties of the product with and without triethylamine, experiments also were made where no triethylamine was used. In an experiment of this type, using 0.2 mole of dimethyldichlorosilane and 0.6 mole of ethylenediamine, a slightly viscous light-yellow liquid was obtained. The elemental analysis of this material indicates a

mixture of the linear and cyclic form. This is shown in the following table:

	Theory For		<u>Found</u>
	<u>Linear Form</u>	<u>Cyclic/Ladder</u>	
% Nitrogen	24.14	16.25	16.8
% Silicon	24.14	32.59	26.2

Based on the silicon analysis, a mixture of about 75% linear and about 25% cyclic and/or ladder is formed in this case.

This work also has shown that other bases such as sodium bicarbonate may be used as acid acceptors in the reaction of dichlorosilanes with diamines.

Elastomers Derived from Silazanes

A polyethylenediaminesilazane was prepared according to the procedure given above where triethylamine was used as the acid acceptor. After the by-product (hydrochloride salt) was removed, the solvent was evaporated to give a "dope" containing about 67% solids. A film was cast on an aluminum plate by using this thick material. The solvent was removed by heating at 70°C for 18 hours, and the resulting film was cured at 204°C for two hours and then at 315°C for one hour. This resulted in a smooth, elastomeric coating which could be peeled from the plate. The film did not appear to be very strong, but it was very elastic. It remained unchanged in physical appearance and retained its elasticity after standing for 17 months under normal atmospheric conditions. After this period, the nitrogen analysis of different areas of the same sample ranged from 0.3 to 13.9% which indicated a heterogeneous composition. This compared to 16.8% nitrogen in the original starting material. This elastomeric material had a smooth, uniform, nonporous surface, and the elastomer was almost transparent. Thicker (1/4-inch) layers of the same material were cured at 400°C in two separate beakers, for one hour in one case and two hours in another. The nitrogen content ranged from 4 to 10% after being cured. The weight loss ranged from 50 to 58%, and the final product was a black foamed solid which was very elastomeric but weak in strength.

It is concluded that silazane polymers of this type may be cured to weak elastomers, and, during the curing process, a variable proportion of the initial Si-N bonding is converted to Si-O bonds. However, the remaining nitrogen content appears to be significant in contributing to the properties of material.

Figure 4 shows a thermogravimetric analysis of the polymer before and after curing. Although the thermal stability is not as good as some of the newer high temperature polymers, this cured silazane-derived material has an attractive degree of thermal stability.

Polymers from Other Diamines

Several other polymers of this type were prepared by reacting dimethyldichlorosilane with various organic diamines. The diamines used included 1,3-propanediamine, 1,6-hexanediamine, 1,4-phenylenediamine, piperazine, benzidine, 4,4'-methylene-dianiline, and 4,4'-oxydianiline. The results and data on these runs are summarized in Table III. The physical form of these polymers included foamed elastomers, rigid foamed solids, powders, waxes, and viscous liquids. Their engineering properties are being investigated presently.

Another series of polymers was prepared by reacting diphenyldichlorosilane with four different organic diamine compounds. The diamines used in this case included ethylenediamine, 1,6-hexanediamine, 1,4-phenylenediamine, and piperazine. The data on these polymers are summarized in Table IV. The physical forms of these polymers ranged from tacky gels to brittle solids. The usefulness of these materials is still under study.

The nitrogen portion of both the phenyl and methyl substituted polymers appears to be somewhat unstable in the atmosphere. An example of this is a case where the diphenylsilane-ethylenediamine polymer was allowed to stand in the air at room temperature overnight and was then placed in an air circulating oven at 250°F for one hour, and then at 400°F for 45 minutes. The elemental analysis of this material is shown before and after heating.

	<u>Found</u>		<u>Theory</u>
	<u>Before Heating</u>	<u>After Heating</u>	
% Carbon	71.8	72.6	70.00
% Hydrogen	6.6	5.5	6.67
% Nitrogen	8.3	1.4	11.67
% Silicon	11.4	14.1	11.66
Unaccounted	1.9	6.4	-

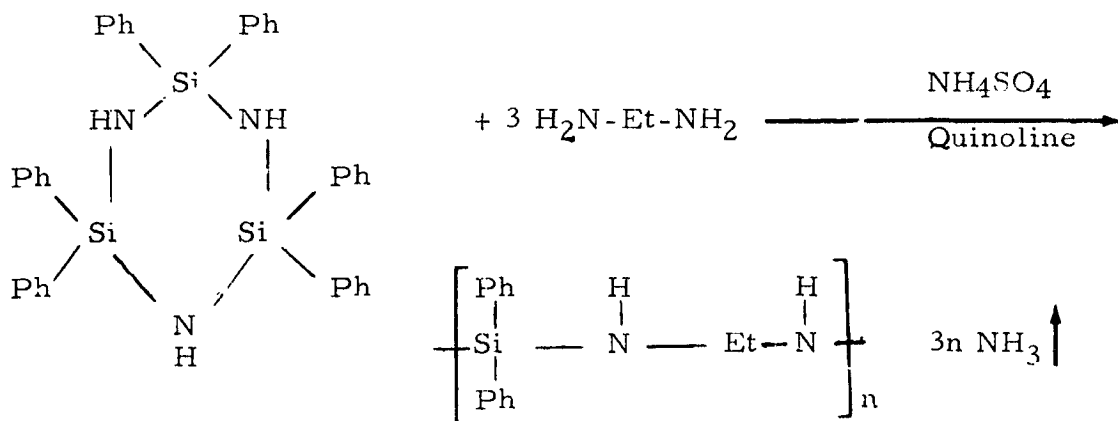
It should be noted that the nitrogen content dropped from 8.3% to 1.4% upon heating in air.

Crosslinking

A number of attempts were made to improve the strength of the cured silane-diamine polymers. The only material that showed any promise was trichlorosilane. When 10% of the dimethyldichlorosilane was replaced by trichlorosilane, a significant improvement in strength of the product was noted. The use of 25% of the trichlorosilane did not appear to increase the strength further. MOCA, (4,4'-methylene-bis-(2-chloroaniline), benzoyl peroxide, and AIBN (α, α' -azodiisobutyronitrile) were not effective as cross-linking agents.

Polymerization of Hexaphenylcyclotrisilazane in the Presence of Diamines

Several attempts were made to copolymerize three different amine compounds with hexaphenylcyclotrisilazane by the catalyzed amine exchange reaction. An example of this type reaction is shown as follows:



Ph represents a phenyl group.

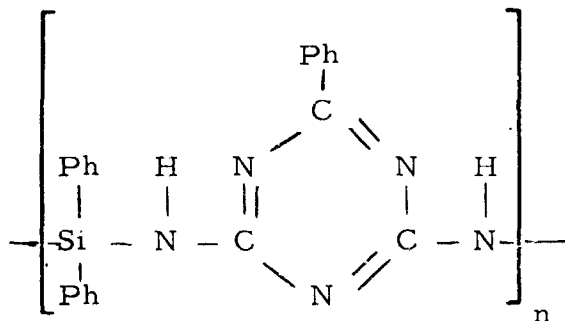
The runs were made by using hydrazine, ethylenediamine, and ethanolamine in quinoline. Ammonium sulfate was used as the catalyst. In each case, the following portions were used:

Hexaphenylcyclotrisilazane	0.017 mole
Amine	0.034 mole
Ammonium Sulfate	0.0019 mole
Quinoline	20 ml

These were heated at about 240°C for 12 to 15 hours. The salts were then removed by filtration, and the polymer was recovered after removing solvent and unreacted amine under reduced pressure. In each case, the product obtained was a hard, glassy solid. Fibers could be drawn from the melt of the ethylenediamine polymer. The preliminary results indicated that the polymers obtained by this route are superior in some respects to those obtained by the halosilane-amine route. Perhaps the main reason for this difference is the elimination of the use of hydrolytically unstable halosilane as an intermediate.

Silazane-Triazine Polymer

A polymer was prepared by the reaction of equal molar amounts of diphenyldichlorosilane and 2,4-amino-6-phenyl-s-triazine using triethylamine as the acid acceptor. A 74% yield of a soft, yellow polymer was obtained. Although it was not possible to fully characterize this polymer, it is believed to have the following structure:

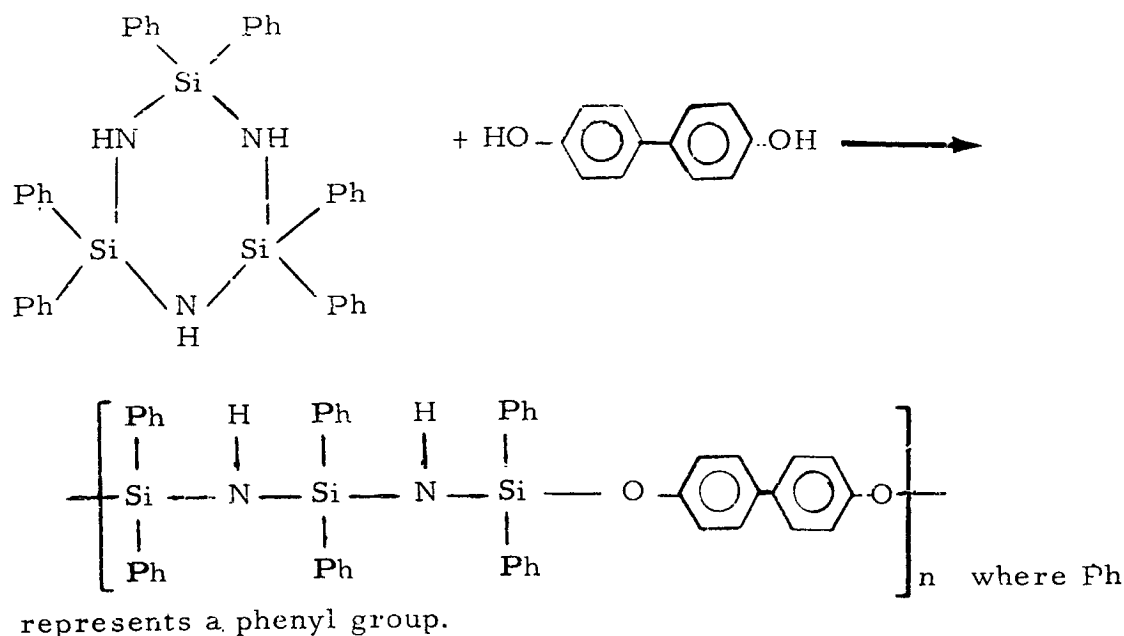


Ph represents a phenyl group.

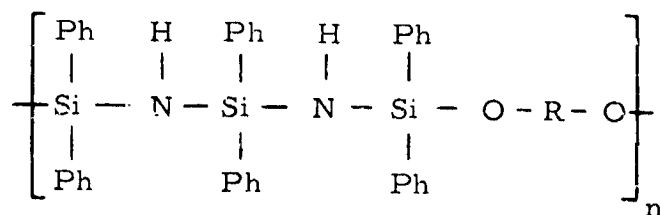
This silazane-triazine structure should have outstanding thermal stability, and this is being studied further.

Silazane-Diol Polymers

Among the most interesting polymers investigated during this study were those obtained by the reaction of hexaphenylphenylcyclotrisilazane with equimolar proportions of various diols. An example of this reaction is shown below:

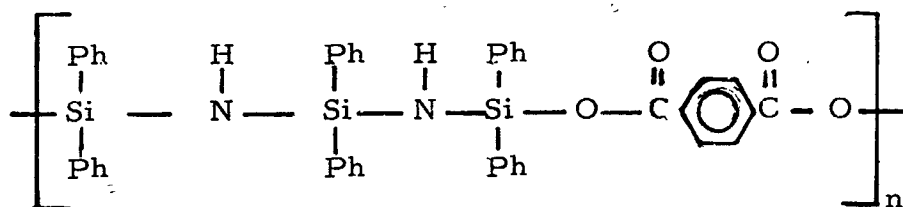


Breed and Elliott (Ref. 13 and 16) have also reported polymers prepared by this method. During this study, we prepared copolymers of hexaphenylcyclotrisilazane with eight different diols. The diols included ethylene glycol, 1,6-hexanediol, hydroquinone, 4,4'-biphenol, 2,2-propane-bis(4-hydroxybenzene), 4,4'-dihydroxydiphenyl ether, 2,7-naphthalenediol, and diphenylsilanediol. Each diol produced a polymer having an empirical analysis consistent with the following general formula:



A number of polymers which are not silazane polymers but which were made by using a silazane as one of the starting materials have been reported (Ref. 17 and 18' by the authors.

A silazane containing polyester was prepared by the melt condensation of equal molar quantities of hexaphenylcyclotrisilazane and terephthalic acid. This produced a polymer believed to have the following structure:



<u>Element</u>	<u>Found</u>	<u>Calculated</u>
% Carbon	70.1	71.31
% Hydrogen	4.2	4.90
% Oxygen	8.7	8.67
% Silicon	11.1	11.37
% Nitrogen	2.7	3.78

Since only ammonia is a by-product of this reaction, the polymerization process is simple and straightforward. A full assessment of the properties of this material will be undertaken.

CONCLUSIONS

The differential thermal analysis of hexaphenylcyclotrisilazane revealed two strong endothermic bands which peaked at about 230°C (melting point 213-215°C) and 550°C, with three additional minor endothermic peaks at approximately 590, 700, and 860°C. The endothermic nature of these changes indicates that this material may be useful as a component in heat-barrier construction. Although there is considerable scatter in the data, there is an indication that the hexaphenylcyclotrisilazane improved the effectiveness of the heat-barrier. The backface temperature rise ranged from 90°C without any hexaphenylcyclotrisilazane to 62°C with 25% hexaphenylcyclotrisilazane. The sample thickness loss ranged from 98 mils with no hexaphenylcyclotrisilazane to 53 mils with 10% hexaphenylcyclotrisilazane.

A one-step method has been developed for the preparation of a solid foamed elastomer from the reaction of dimethyldichlorosilane and ethylenediamine. This material subsequently has been cured into a stable, transparent, elastomeric film having low strength but attractive thermal stability. A number of related polymers were prepared by reacting dimethyldichlorosilane with other organic diamines. An analogous series of polymers with phenyl substitution on the silicon atoms was prepared by the reaction of diphenyldichlorosilane with organic diamines. When cured at 400°C, these materials form very stable elastomeric products. A considerable amount of Si-N bonding is converted to Si-O bonding during the curing process. However, it is concluded that the amount of Si-N bonding remaining plays a significant part in the properties of these materials.

A number of attempts to improve the strength of the cured elastomers has resulted in slight increases in strength. However, this increase has not been of sufficient significance to produce a material with outstanding engineering properties.

A number of potentially useful polymers was prepared by chain opening reactions between equimolar amounts of hexaphenylsilazane and various diol compounds. Some of these materials have good film and

fiber-forming properties. The best of these materials is stable to about 500°C and undergoes a total weight loss of about 45% during heating to 900°C.

An interesting new polymer which contains the triazine ring was prepared by linking the rings through the -N-Si-N- linkage. Many possible variations exist for polymers of this type.

A polymer containing polyester units along with silicon-nitrogen bonds was also prepared.

These exploratory studies have served to demonstrate the many different types of silazane polymers that are within reach by established synthetic routes. These materials are characterized by high thermal stability and varying degrees of hydrolytic instability. The utility of simpler silazane compounds as synthetic intermediates has also been demonstrated by this work.

Continued study of these materials as high temperature or intumescent coating constituents is indicated. An evaluation of the more promising elastomeric materials derived from silazanes will also be attempted.

TABLE I
COMPOSITION OF HEAT-BARRIER SAMPLES (1)

Sample	Silastic 651-U (%)	Hexaphenyl- cyclotri- silazane (%)	Pyroshield- 21 (%)	Benzoyl Peroxide (%)	Curing Time at 260°F (Minutes)	Thickness of Samples (Mils)
A	100	-	-	0.4	5	373
B	96	4	-	0.4	5	405
C	90	10	-	0.36	2	395
D	90	10	-	0.36	5	395
E	80	10	10	0.32	5	390
F	75	25	-	0.32	5	393

(1) Prepared by Southern Research Institute, Contract NAS8-1510.

TABLE II

TEST RESULTS OF HEAT-BARRIER SAMPLES

Exposure to radiant lamp at 24 BTU/ft²/sec for 120 seconds;
vibrated at 30 cycles per second with displacement of 0.25
inch; acceleration of 11 times gravity.

Sample	Back Face Temperature Rise at Cut Off (°C)	Smoke Began at Seconds	Flaming Began at Seconds	Thickness Loss (Mils)
A	90.0	4	10	98
B	62.8	4	12	55
C	76.7	4	7	60
D	70.5	5	8	53
E	83.9	3	6	All
F	62.2	4	6	68

TABLE III

POLYMERS FROM DIMETHYLDICHLOROSILANE AND ORGANIC DIAMINES

Triethylamine was used as the acid acceptor except as noted

Diamine Used	Yield % of Theory	Physical Form of Polymer	Elemental Analysis								
			% Found				% Calculated				
			C	H	N	Si	Remaining	C	H	N	Si
(1)											
1,3-propane- diamine	76.2	Liquid, slightly viscous	36.8	9.2	13.9	26.9	13.2	45.10	9.73	15.03	30.14
1,6-hexane diamine	38.7	Sticky, rubbery solid	47.9	10.7	11.8	18.9	10.7	55.81	11.63	16.28	16:28
Benzidine	3.8	Peach colored powder	50.3	6.8	6.6	18.5	17.8	70.00	6.67	11.67	11.66
1,4-phenylene- diamine	7.9	Sticky solid	54.6	7.0	16.5	16.0	5.9	58.54	7.32	17.07	17.07
4,4'-methylene- dianiline	87.0	Foamed Elastomer	69.9	6.7	10.3	9.7	3.4	70.87	7.09	11.02	11.02
Piperazine	68.5	Waxy solid	41.8	8.5	14.4	20.1	15.2	52.17	7.25	20.29	20.29
4,4'-oxydianiline	—	Soft foamed solid	68.2	6.4	10.0	8.3	7.1 ⁽²⁾	65.60	6.28	10.92	10.96 ⁽²⁾

(1) The excess diamine was used as the acid acceptor.

(2) The theory for oxygen in this polymer is 6.24%.


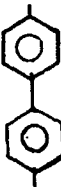
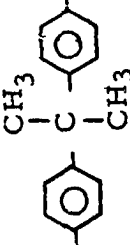
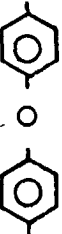

TABLE IV

POLYMERS FROM DIPHENYLDICHLOROSILANE AND ORGANIC DIAMINES

Diamine Used	Yield, % of Theory	Physical Form of Polymer	Elemental Analysis								
			% Found				% Calculated				
			C	H	N	Si	Remaining	C	H	N	Si
1,3-propane- diamine	—	Tacky Gel	71.9	6.6	3.3	11.4	1.8	70.0	6.7	11.7	11.6
1,6-hexane- diamine	—	Tacky Gel	69.5	7.2	6.5	9.4	7.4	73.0	8.1	9.5	9.5
1,4-phenylene- diamine	55.4	Crystal- line Solid	74.3	5.7	9.4	7.5	3.1	75.0	5.6	9.7	9.7
Piperazine	94.5	Brittle Solid	67.5	6.2	5.9	10.2	10.2	73.3	5.3	10.7	10.7

TABLE 7

POLYMERS FROM HEXAPHENYLCYCLOTRISILAZANE AND DIOL COMPOUNDS

20 sps		Fiber and/or Film Forming Properties	
Formula for R	Physical Form	Fiber and/or Film Forming Properties	
$\begin{array}{c} \text{Ph} \\ \\ -\text{Si}- \\ \\ \text{Ph} \end{array}$	Brittle, glassy, milky-white solid	Very weak and brittle film	
$-(\text{CH}_2)-$	Light brown, sticky, elastomeric semisolid	None formed	
$-(\text{CH}_2)_6-$	Light brown, elastomeric solid	Fairly weak elastomeric fiber	
	Light brown, glassy solid	Weak semiflexible fibers, brittle film	
	Tan, semiflexible, tough solid	Fairly strong flexible fibers and film	
	Brittle solid	Weak and brittle fiber	
	Brittle, glassy, light tan solid	Semi flexible fairly strong fiber	
	Brittle, glassy, amber brown solid	Weak brittle film	

(1) Ph represents a phenyl group.

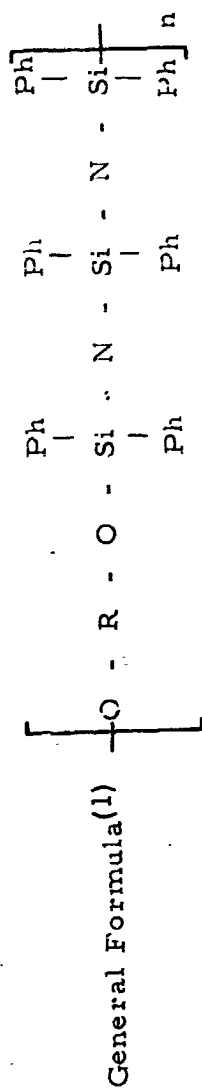
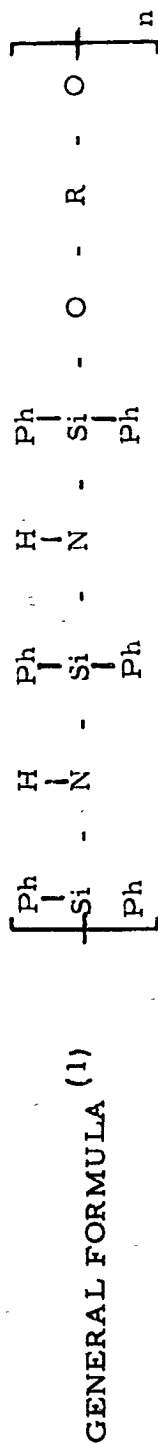


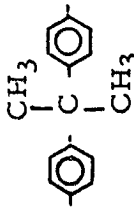
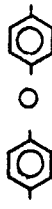



TABLE VI
CHEMICAL ANALYSIS OF POLYMERS FROM HEXAPHENYLCYCLOTRISILAZANE
AND DIOL COMPOUNDS



Formula for R'	Elemental Analysis									
	% Found					% Calculated				
	C	H	O	N	Si	C	H	O	N	Si
$\begin{array}{c} \text{Ph} \\ \\ -\text{Si}- \\ \\ \text{Ph} \end{array}$	71.2	5.2	3.9	2.7	14.7	72.91	5.32	4.05	3.54	14.18
$-(\text{CH}_2)_2-$	68.7	5.8	8.0	0.2	11.5	69.51	5.49	4.88	7.32	12.80
$-(\text{CH}_2)_6-$	72.6	6.2	3.4	2.3	12.4	72.83	6.36	4.62	4.05	12.14
	73.2	5.0	-	4.1	12.9	73.69	5.26	4.68	4.09	12.28
	76.2	5.1	6.3	1.8	10.7	75.79	5.26	4.21	3.68	11.05
	75.5	5.5	3.7	3.4	11.2	76.50	5.50	4.00	3.50	10.50
	74.8	5.2	8.1	2.4	11.0	74.23	5.15	6.19	3.61	10.82
	75.4	5.0	5.9	2.9	11.8	75.20	5.18	4.36	3.82	11.44

(1) Ph represents a phenyl group.

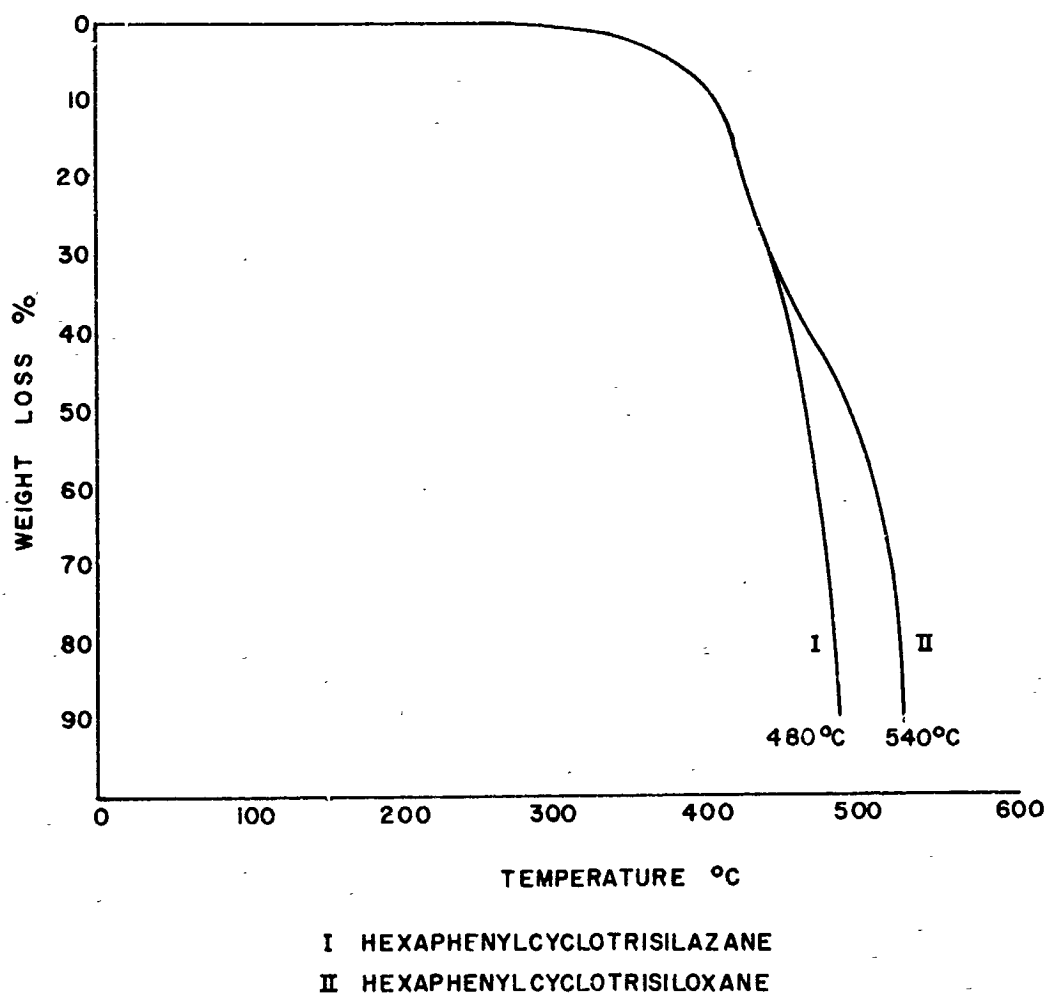


FIGURE I THERMOGRAVIMETRIC ANALYSIS OF CYCLIC TRISILAZANES

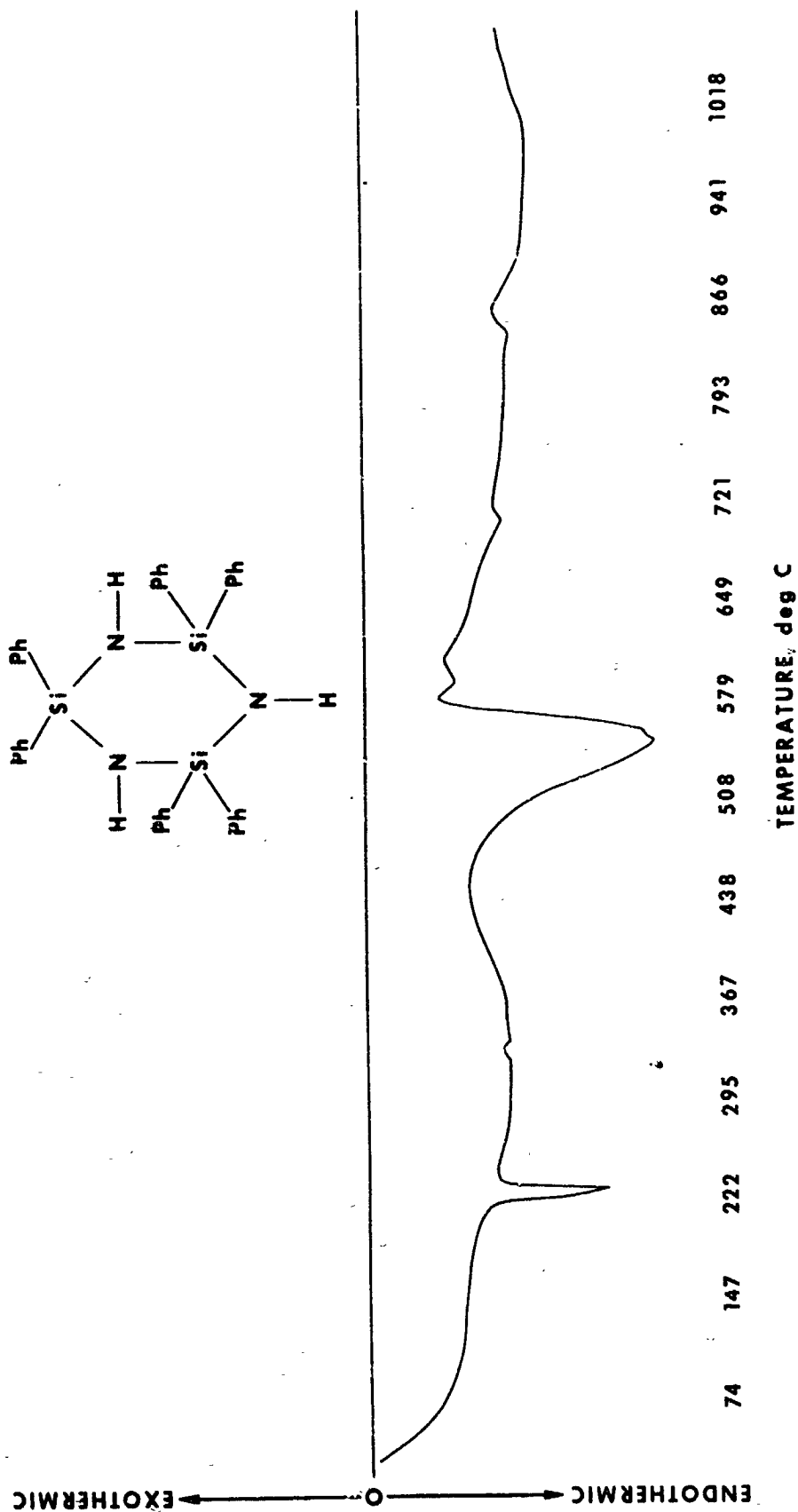


FIGURE 2 DIFFERENTIAL THERMAL ANALYSIS OF HEXAPHENYLCYCLOTRISILAZANE

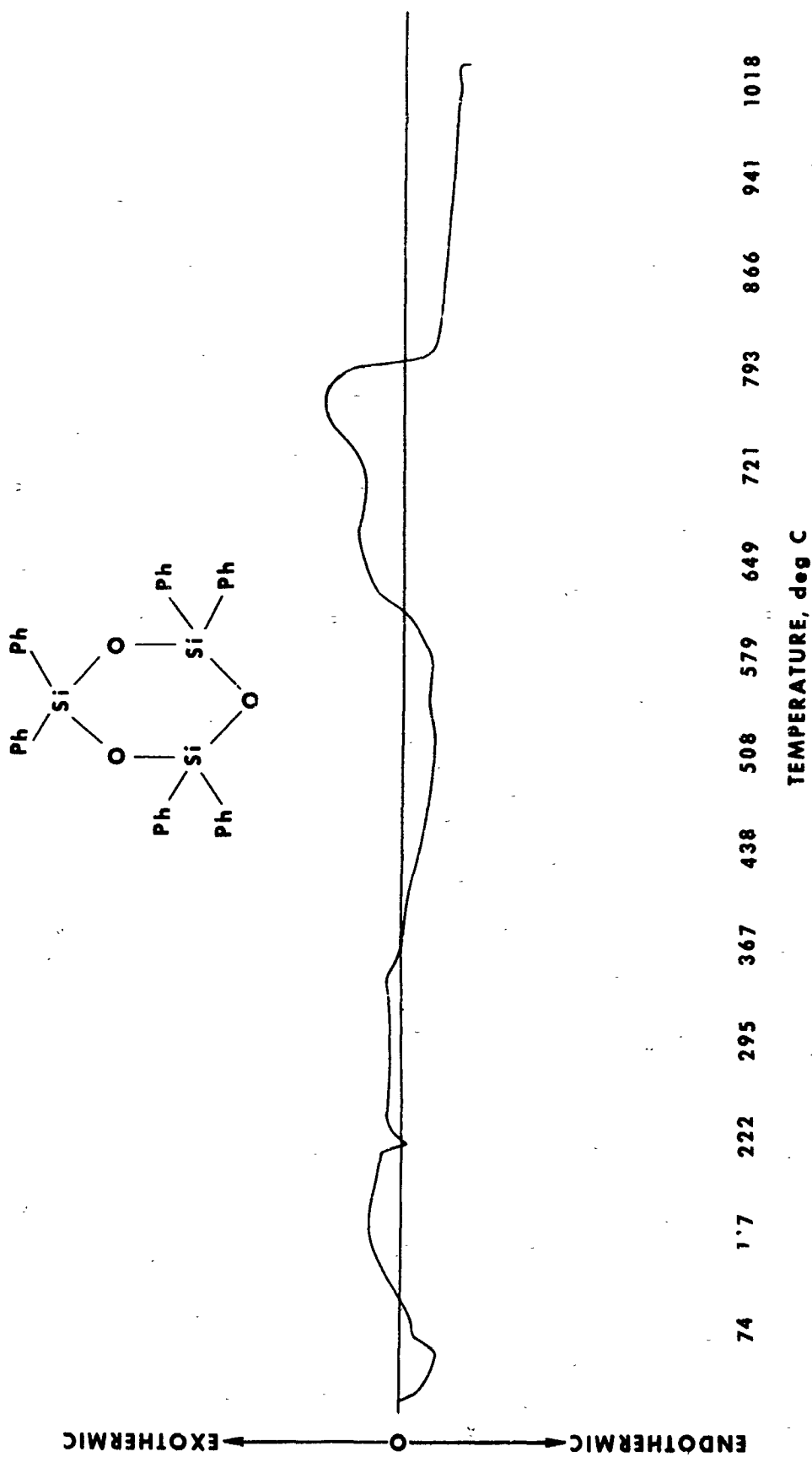


FIGURE 3 DIFFERENTIAL THERMAL ANALYSIS OF HEXAPHENYLCYCLOTRISILOXANE

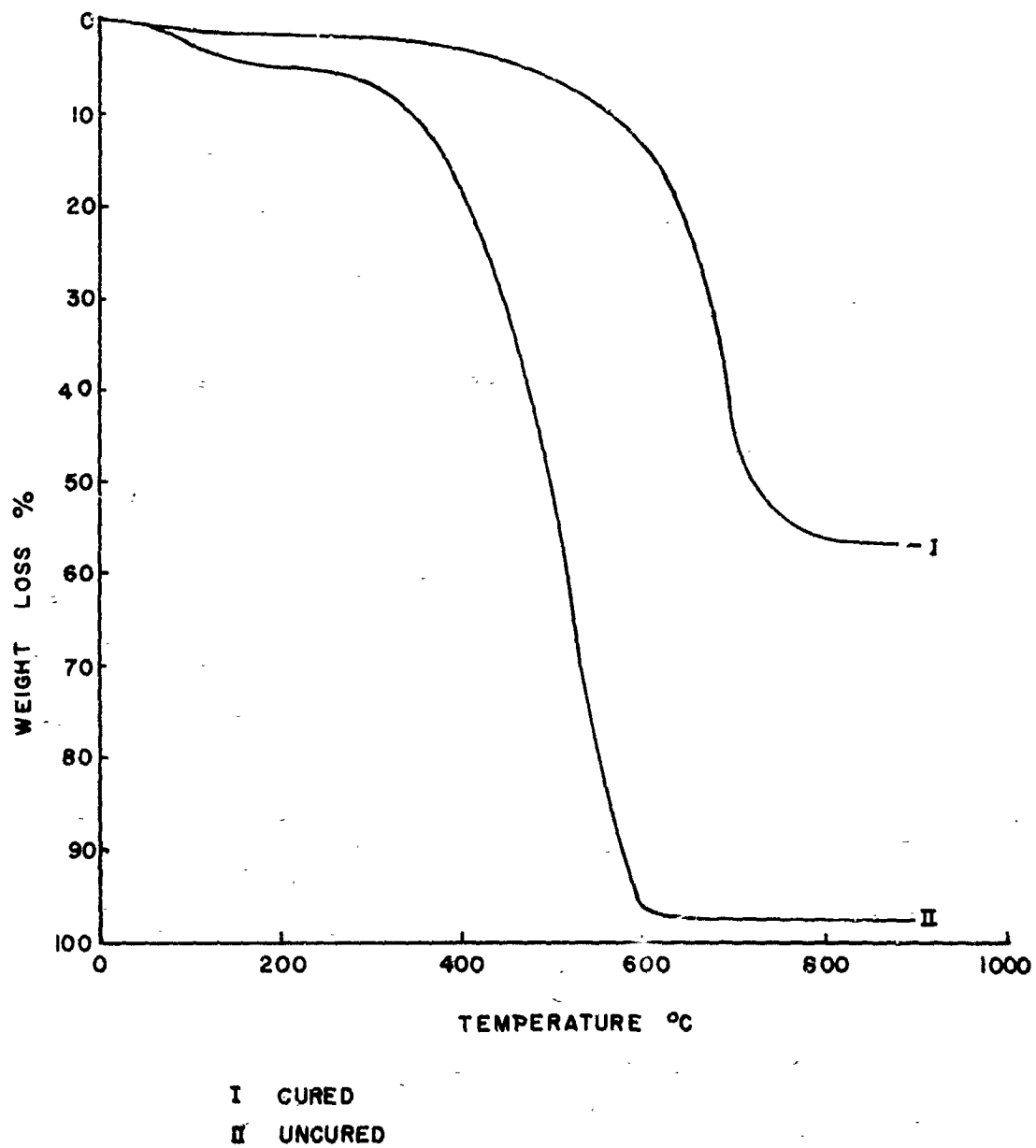
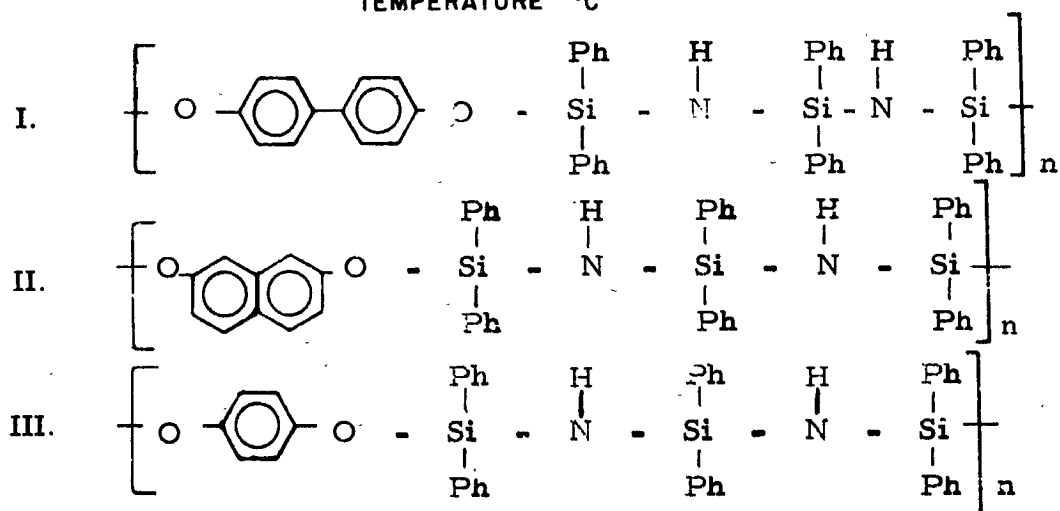
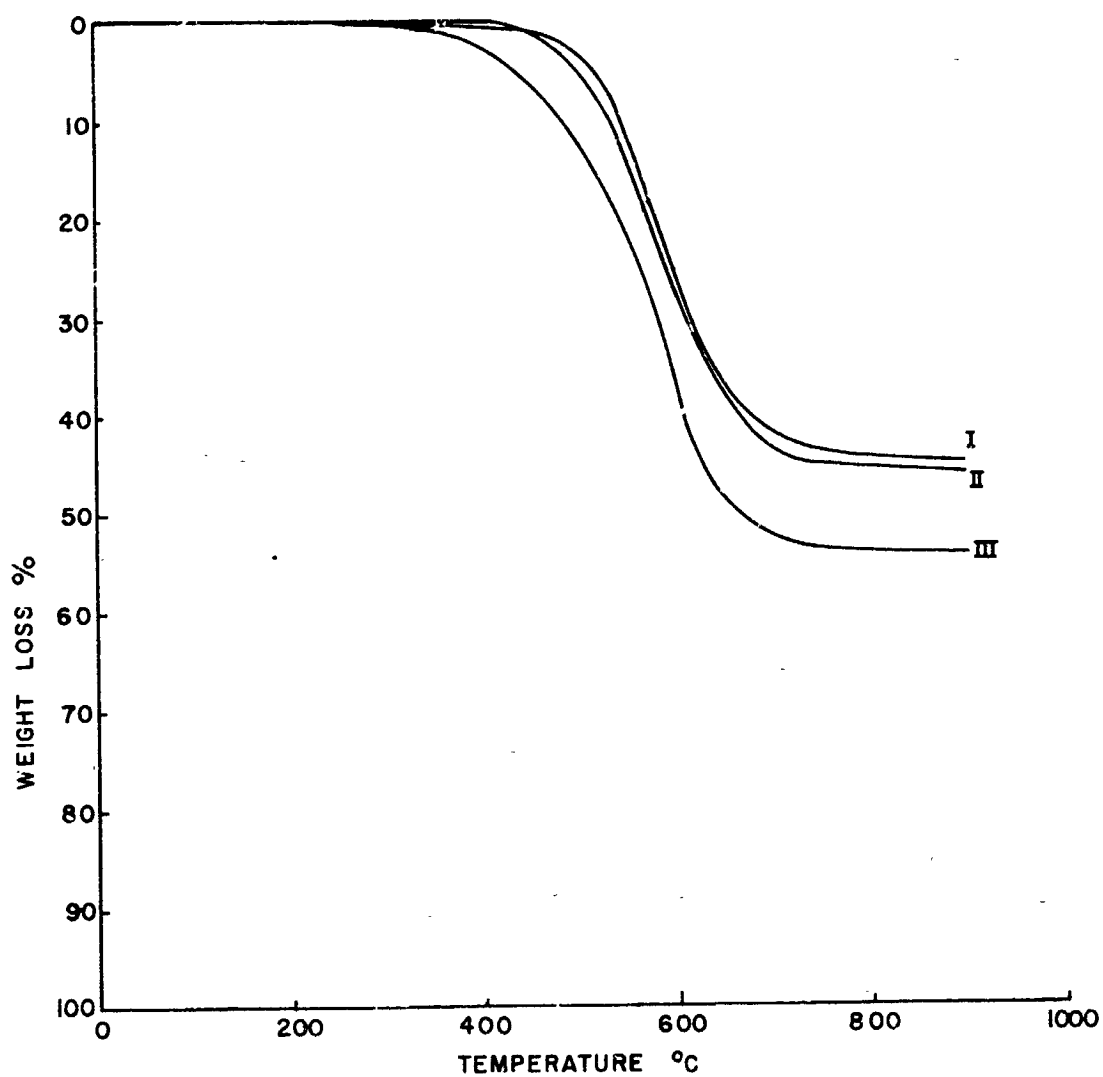
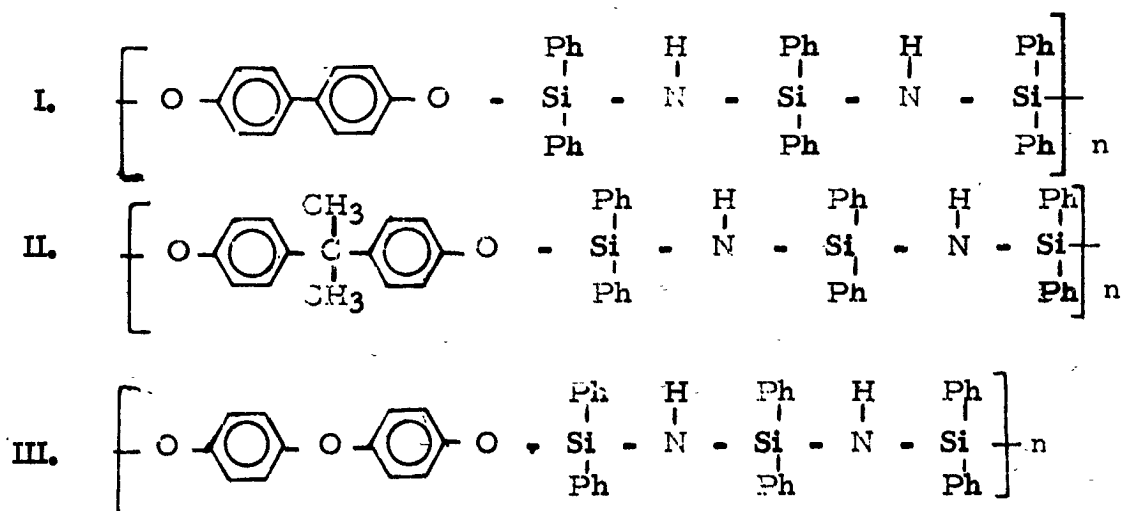
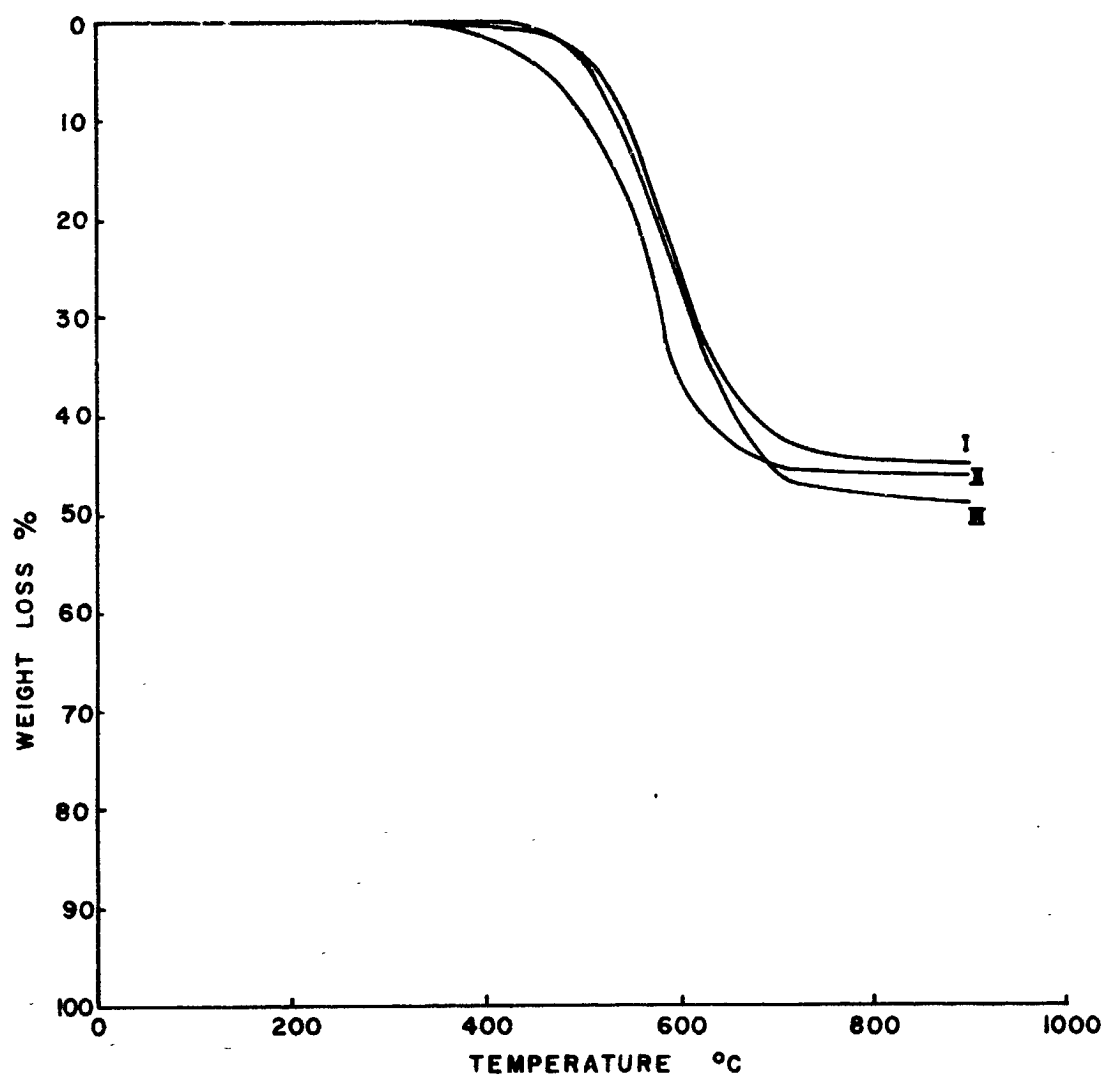


FIGURE 4- THERMOGRAVIMETRIC ANALYSIS OF ETHYLENEDIAMINE-SILAZANE POLYMER



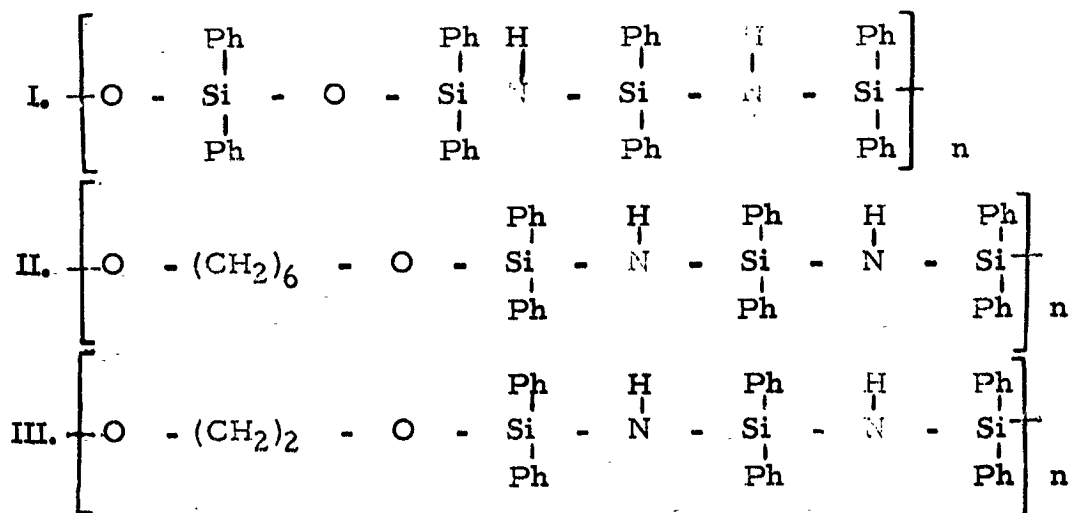
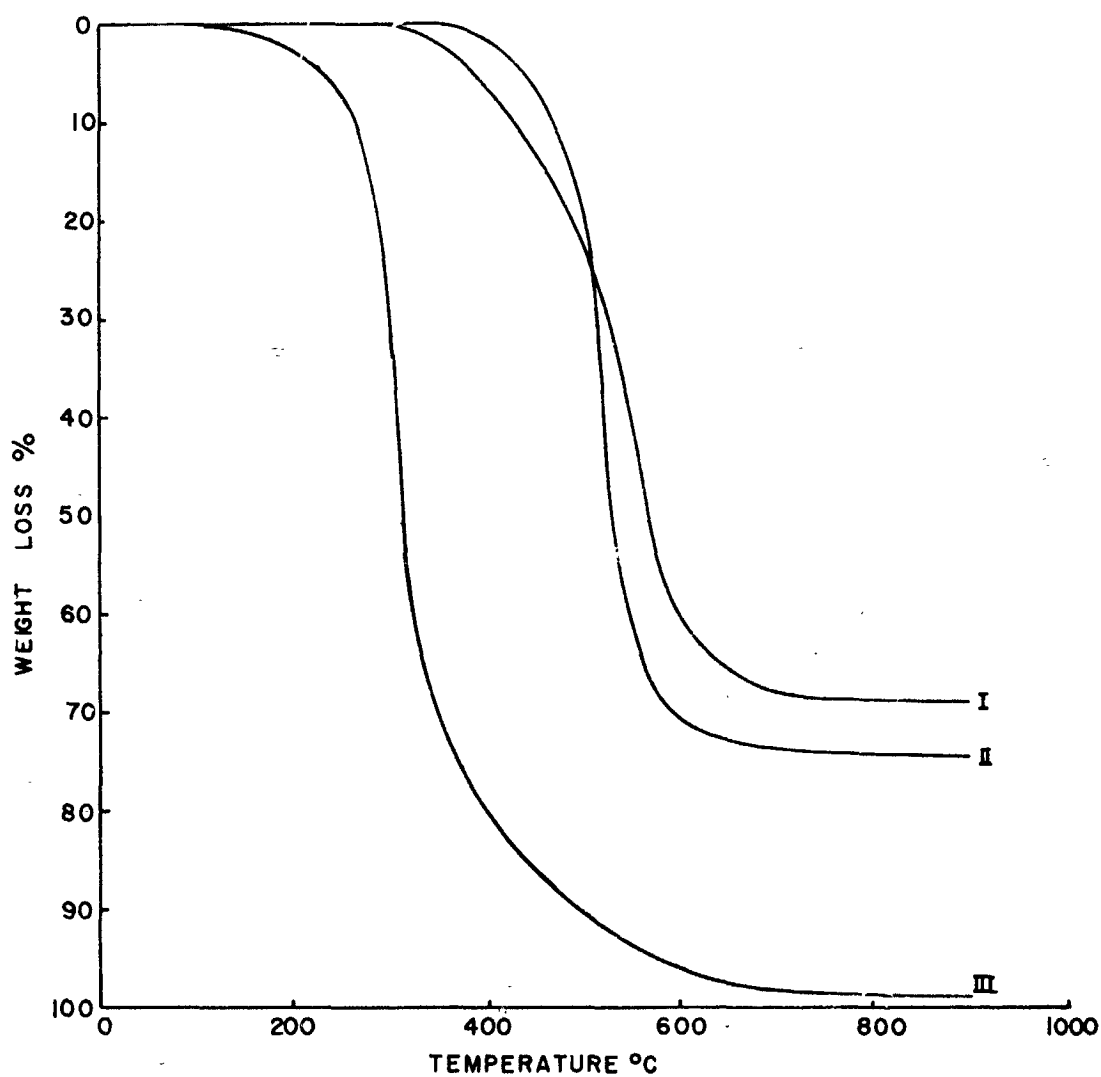
Ph represents a phenyl group.

FIGURE 5. THERMOGRAVIMETRIC ANALYSIS



Ph represents a phenyl group in each case.

FIGURE 6. THERMOGRAVIMETRIC ANALYSIS



Ph represents a phenyl group in each case.

FIGURE 7. THERMOGRAVIMETRIC ANALYSIS

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